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**Preparation of Non-Oxide Ceramics by
Pyrolysis of Organometallic Precursors**

by

L.V. Interrante, W.R. Schmidt, P.S. Marchetti and G.E. Maciel

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**Department of Chemistry
Rensselaer Polytechnic Institute
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PREPARATION OF NON-OXIDE CERAMICS BY PYROLYSIS OF ORGANOMETALLIC PRECURSORS

LEONARD V. INTERRANTE[§], WAYDE R. SCHMIDT[§], PAUL S. MARCHETTI[¶], and GARY E. MACIEL[¶], [§]Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180-3590; [¶]Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

INTRODUCTION

Chemical processing routes to advanced ceramic materials are gaining importance as a convenient approach to control the stoichiometry, purity, microstructure and final form of the ceramic products [1]. The pyrolytic conversion of organometallic molecules and polymers is one such chemical processing route that has been widely applied in ceramic fiber technology [1,2], in coating processes [1,2], and in the sintering of bulk ceramic objects [3]. Despite these advances in practical applications, there is a continuing need in this area for a better fundamental understanding of the chemistry involved during the precursor-to-ceramic conversion process and for the development of new precursors which yield the desired ceramic(s) in high yield and purity.

The recent discovery of superplasticity for nanocrystalline SiC/Si₃N₄ obtained by pyrolysis of a methylsilazane [4], along with the potential advantages afforded by nanocrystalline materials in terms of mechanical, optical, and electronic properties [5], has focused attention on the preparation of these materials by pyrolysis of molecular precursors. Finally, the prospect of developing ceramic powders and/or films with controlled nanoporosity for use as catalysts, catalyst supports and as gas separation media offers additional incentive to develop further the range of processes and new systems available through polymer precursor pyrolysis [6].

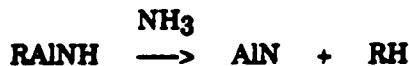
This paper focuses on our own efforts over the past ca. 10 years to explore polymer/molecular precursor pyrolysis as a route to both known and potentially new non-oxide ceramic compositions with unique properties.

Organometallic Precursor Routes to AlN

Our efforts in this area began with an attempt to obtain AlN powder in high yield and purity from organoaluminum-ammonia derivatives. These experiments led to a process for AlN powder production that employs Et₃Al and NH₃ as the Al and N sources, respectively (Scheme I), and which gives a high surface area, pure AlN powder in nearly quantitative yield at a low net



Scheme I



materials cost [7]. A key step in this procedure is the use of an NH₃ atmosphere in the final stage of conversion to promote loss of residual alkyl groups as volatile hydrocarbons, thereby yielding stoichiometric AlN with both C and O contents less than 0.1 wt. % and negligible amounts of other impurities. This is to be contrasted with alternative processing methods that start with Al or Al₂O₃ where control of product stoichiometry and/or C and O content is problematic.

The use of Me₃Al as the Al source in this same sequence of reactions involving NH₃ yields [Me₂AlNH₂]₃ as a crystalline intermediate. This compound is relatively volatile and serves as an excellent single-source precursor for AlN CVD yielding high quality, polycrystalline AlN films at relatively low deposition temperatures (ca. 500 °C) compared to alternative mixed Al and N

precursor systems, such as AlX_3 ($X = Cl, Br$) or Me_3Al and NH_3 [8]. In this case, the loss of C from the growing AlN surface is relatively efficient, leading to low levels of C incorporation in the product films even without the use of additional NH_3 as a co-reactant.

These applications of the $R_3Al + NH_3$ system as a source of AlN powder and thin film have been aided and enhanced by our continuing studies of the chemistry represented in the sequence of reactions shown in Scheme I. This work has included kinetic studies of the $Me_3Al:NH_3$ decomposition to $[Me_2AlNH_2]_3$, which provided the first indirect evidence for a trimer (T) \rightleftharpoons dimer (D) \rightleftharpoons monomer (M) equilibrium for the Me_2AlNH_2 product species [9]. The existence of at least the T \rightleftharpoons D equilibrium in hydrocarbon solution was evidenced in further NMR studies of the $R = Me, Et, i-Bu$ and $t-Bu$ derivatives which yielded the respective ΔH and ΔS values [10]. Our isolation of the trimeric form of the $[(t-Bu)_2AlNH_2]_3$ compound led to a crystal structure study that revealed a novel planar arrangement for the $(AlN)_3$ six-membered ring [11]. In this study, the factors that determined the relative stabilities of the dimer and trimer forms for the $[R_2AlNH_2]_n$ compounds, as well as the conformation of the $[R_2AlNH_2]_3$ ring system, were noted and discussed [11]. A subsequent theoretical study indicated a probable planar structure for the monomeric Me_2AlNH_2 species and led to a prediction of its bond lengths and angles [12]. Time of flight studies of the $[Me_2AlNH_2]_3$ system have recently confirmed the existence of dimeric and trimeric forms in the vapor phase [13]; however, the corresponding monomeric form currently remains elusive.

An alternative solution-based route to AlN films and coatings which employs a mixture of R_3Al and ethylenediamine (en) has also been investigated yielding, in the case of the 2:1 $R_3Al:en$ system, a soluble polymeric intermediate $[(R_2Al)_2(en-2H)]_n$ which was used to make AlN films on Si [14]. Again, a detailed study of the chemistry involved in the conversion of the $xR_3Al:en$ ($x = 2, 1$) adducts to polymeric products was carried out which has revealed a series of novel aluminum/(en-2H) cluster intermediates on thermolysis of the 1:1 adducts [15].

Precursors to SiC and Si₃N₄

Our efforts to synthesize new SiC precursors were prompted by the problem of excess C in SiC derived from most of the organosilicon polymers that are currently employed as precursors. These precursors typically contain a 2/1 or greater ratio of C/Si initially, and the excess C is not eliminated cleanly as hydrocarbons on pyrolysis. Residual carbon can lead to decreased oxidative stability for the resulting SiC ceramics, as well as excessive creep and other undesirable effects on the microstructure and/or properties. Moreover, in the presence of oxygen derived from curing, handling, and/or partial oxidation of the precursors or from oxide components in a composite, loss of CO_x species becomes a significant problem for these materials beyond about 1200 °C [16].

For these reasons, we have directed our attention to the preparation of polycarbosilanes that have a nominal "SiH₂CH₂" composition and have explored two approaches to such polymers that yield structurally quite different products having either highly branched or linear -Si-CH₂-Si- backbones. Both polymers were found to have high ceramic yields after thermal processing and gave near-stoichiometric SiC on pyrolysis in N₂.

The first approach developed employs Mg as a coupling agent and Cl_3SiCH_2Cl as the starting material. The resultant "chloropolymer" (nominally, "[SiCl₂CH₂]") was converted to the hydridopolycarbosilane (HPCS) "[SiH₂CH₂]" by reduction with $LiAlH_4$. A side reaction with the diethylether solvent leads to the incorporation of a small amount of ethyl groups, giving the actual formula, $[SiH_{1.85}Et_{0.15}CH_2]$ [17].

A structural analysis of this polymer by solution NMR methods has revealed a complex, highly branched structure, resulting from the ternary functionality of the Cl_3Si end of the monomer unit. Despite this branching, the polymer is not appreciably crosslinked and remains liquid and highly soluble in hydrocarbon solvents. This "[SiH₂CH₂]" polymer undergoes crosslinking through loss of H₂ above ca. 200 °C. Additional crosslinking by thermal treatment produces a gel at 200 °C (12 hrs) and an insoluble rubber at 400 °C (2 hrs), which have significantly increased ceramic yields (53% and 91%, respectively) on pyrolysis in N₂ to 1000 °C (Figure 1), as compared to the initially isolated, untreated polymer (30-40% ceramic yield) [18].



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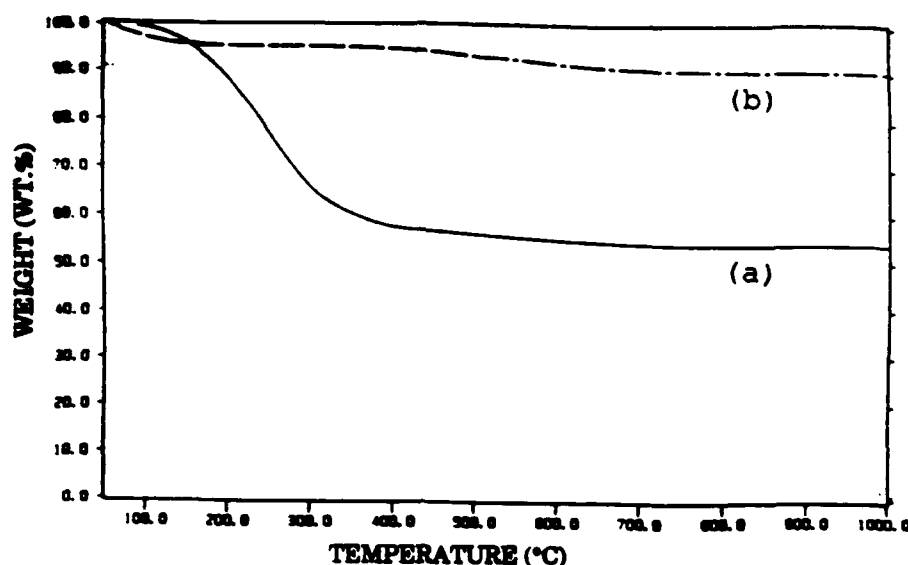


Figure 1. TGA curves for highly branched hydridopolycarbosilane (HPCS) after thermal crosslinking a) 200 °C (12 hrs), b) 400 °C (2 hr).

We have used this polymer to obtain amorphous "SiC" coatings on glassy carbon substrates and C fiber that inhibit oxidation of these substrates at 600 °C in air. Adherent coatings have also been applied to various metal surfaces, including C-steels. These coatings can be applied as polymer solutions through dip or spin coating techniques, followed by pyrolysis to 1000 °C in N₂. We have also used this hydridopolycarbosilane to prepare particulate and fiber-reinforced SiC/SiC composites by liquid phase impregnation. The advantages over alternative precursors for SiC include the effective elimination of excess C and O, thereby providing a SiC product that is more thermally and oxidatively stable than those obtained using alternative precursors [19]. This polymer also does not require a catalyst or an oxidation step for thermosetting and exhibits a high ceramic yield of essentially pure SiC.

The second approach that we have developed to obtain a "[SiH₂CH₂]" polymer involves the ring-opening polymerization (ROP) of tetrachlorodisilacyclobutane, [SiCl₂CH₂]₂ [20]. The resultant "chloropolymer" is again reduced to the hydridopolymer with LiAlH₄. In this case, however, the product polycarbosilane is a high molecular weight linear polymer with [SiH₂CH₂]_n as the actual repeat unit. This polymer is also a liquid at room temperature, is soluble in hydrocarbons, and undergoes pyrolysis under N₂ to give stoichiometric SiC in yields approaching the theoretical value (up to 91%) by 1000 °C. This polymer is currently available only in small quantities by a relatively low yield process and is not expected to be competitive in the short term with the branched "[SiH₂CH₂]" polymer as a source of SiC for practical applications.

Both of these synthetic methods are fundamentally new approaches for preparing useful polymeric precursors to SiC. These polycarbosilanes undergo a novel, thermally-induced crosslinking process that involves elimination of H₂ from SiH_n groups on the polymer backbone. They show considerable promise as high yield precursors to stoichiometric SiC and, in the case of the branched polymer, as a viable source of SiC coatings and matrices for composites.

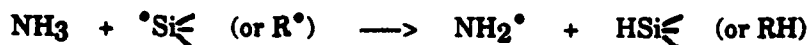
In addition to these ongoing investigations of the pyrolysis of our own "SiH₂CH₂" polymers, we have carried out parallel studies of a commercial polysilane of the approximate composition,



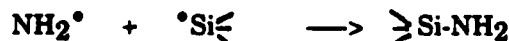
obtained from Union Carbide (Y-12044) [19,21]. This liquid polymer provides a predominantly polysilane $(-RR'Si-)_n$ chain structure with reactive vinyl and H groups for possible thermosetting through radical coupling of the vinyl groups and hydrosilylation. It is known to yield a C-rich (ca. 17 wt.% excess C) SiC on pyrolysis in N_2 or other inert atmospheres. We have studied the crosslinking process and the evolution of the SiC network structure in this polymer by a combination of methods, but of particular value has been the use of solid state NMR methods, where the Si, C and even H environments in the precursor were followed through the different stages of the thermal conversion process [21]. The chief conclusion in the case of the pyrolysis in N_2 was that cleavage of the end groups from the polymer backbone to give R_3Si^\bullet radicals at relatively low temperature is a key step in both the thermosetting and the initial part of the polymer conversion process, during which the $-Si-Si-$ backbone converts to $-Si-CH_2-Si-$ via a radical-initiated $-CH_2$ insertion process [21].

Following other studies in which NH_3 has been used to convert polycarbosilanes and polysilazanes to Si_3N_4 , we have found that the vinylic polysilane and our " SiH_2CH_2 " polymer can be used to obtain high surface area powders of largely amorphous Si_3N_4 at $1000^\circ C$ [22]. The Si_3N_4 eventually crystallizes with reduction in surface area on further heating above $1200^\circ C$; however, below this temperature, in the absence of certain impurities such as B or BN [23], this high surface area Si_3N_4 is relatively stable and conceivably could be used as a catalyst support [6].

We have recently completed a detailed study of the chemistry occurring during the conversion of this vinylic polysilane to Si_3N_4 in NH_3 that has included esr and dynamic nuclear polarization, as well as solid state NMR measurements on the intermediate and final solid products [24]. A key difference here with respect to the analogous conversion in N_2 , in addition to the eventual loss of all C and its replacement by N, is the relatively low spin concentrations for the samples pyrolyzed in NH_3 (Figure 2). Whereas the "inert" atmosphere pyrolysis generates a significant concentration of paramagnetic centers and unpaired spins in the solid products, in NH_3 the unpaired spins are effectively quenched, presumably by radical transfer processes involving NH_3 (Scheme II).



Scheme II



The resultant NH_2^\bullet radicals generated can couple with Si-based radical sites on the polymer backbone. This process, along with nucleophilic attack of NH_3 directly on the backbone Si atoms of the polymer, are believed to be responsible for the efficient removal of C, as hydrocarbons, and its replacement by NH_x species. Condensation processes that eliminate NH_3 and silylamine species then lead to the extended $-Si-N-$ network structure of Si_3N_4 [24].

A study of the condensation polymerization and pyrolysis of silicon tetradiethylamide, $[Si(NEt_2)_4]$, was also carried out with the aid of solid state ^{29}Si , ^{13}C , and 1H (CRAMPS) NMR spectroscopy [25]. Among the key observations here was that the initial SiN_4 bonding of the precursor was maintained throughout the conversion of the tetraamide to the polymeric silazane and then to the amorphous preceramic product at $800^\circ C$, albeit with the formation of a considerable amount of free C by-product. On heating further to $1500-1600^\circ C$, this amorphous "silicon nitride" plus C mixture is converted under an Ar atmosphere largely to SiC and $N_2(g)$, whereas under one atmosphere of N_2 , crystalline $\alpha-Si_3N_4$, along with free C, are the main products.

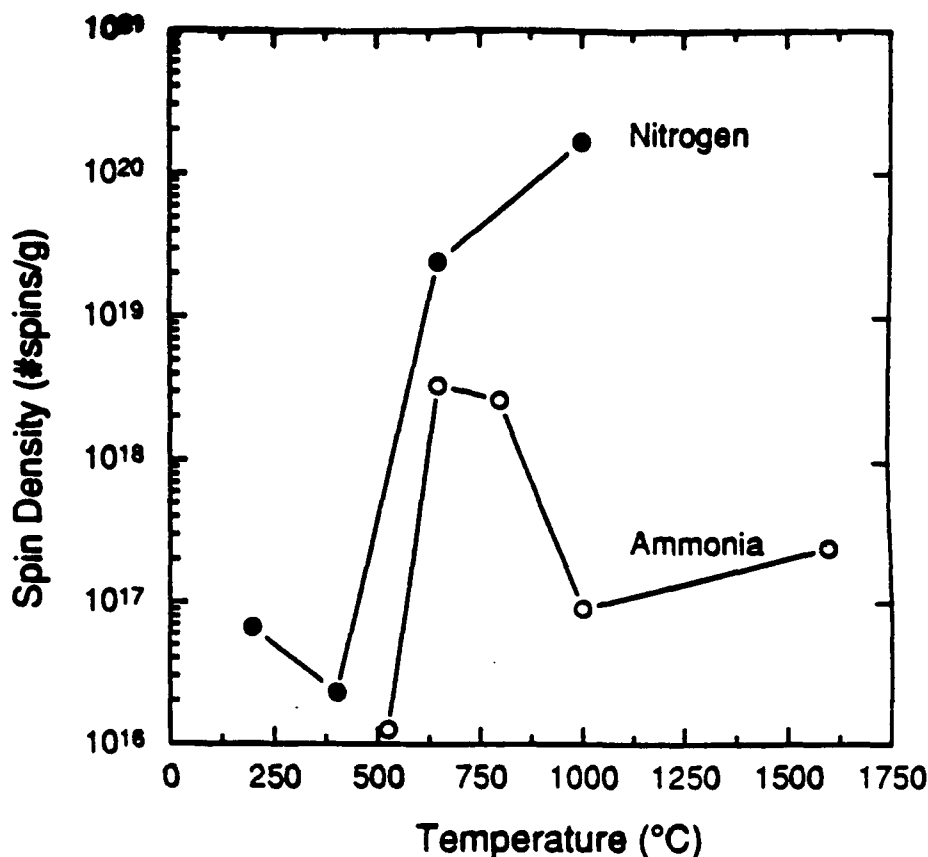


Figure 2. Spin densities as a function of temperature for solids isolated by pyrolysis of the vinylic polysilane in either nitrogen or ammonia.

Preparation of AlN/SiC Solid Solutions and Ceramic Nanocomposites Using Organometallic Precursors

We have found that both homogeneous solid solutions and nanoscale composite mixtures of SiC with AlN can be obtained on pyrolysis of mixtures of the polycarbosilanes or polysilane (as the SiC source) and dialkylaluminum amides (as the AlN precursor) and that the ceramic yield of the polycarbosilane is greatly enhanced in the presence of the AlN precursor [26].

In this work the use of miscible liquid precursors to both AlN and SiC allowed the attainment of molecular-level homogeneity in the initial precursor mixture. Subtle differences in the extent to which this molecular-level homogeneity was maintained after pyrolysis of the precursor mixture were evidenced by X-ray diffraction studies and solid state ^{27}Al and ^{29}Si NMR spectroscopy. Figure 3 shows a series of X-ray diffraction patterns of a 50/50 mole % mixture of the completely miscible liquid HPCS and $[\text{Me}_2\text{AlNH}_2]_3$ precursors which were pyrolyzed gradually to 1000 °C (GP) (Fig. 3a) or rapidly pyrolyzed at 500 °C (RP) prior to further heating (Fig. 3b). These samples were further heated in N_2 to temperatures as high as 1800 °C to crystallize the solid solution. In both cases the X-ray diffraction patterns obtained at 1800 °C are consistent with expectations for the 2H solid solution [26,27]; however, the sharper lines exhibited by the rapidly pyrolyzed sample suggest that the crystallinity is somewhat higher in this case as compared to the gradually pyrolyzed sample. These XRD patterns contrast markedly with that

obtained on pyrolysis, and subsequent annealing at 1800 °C, of the HPCS polymer alone. In this case the diffraction pattern is consistent with expectations for the cubic 3C form of SiC.

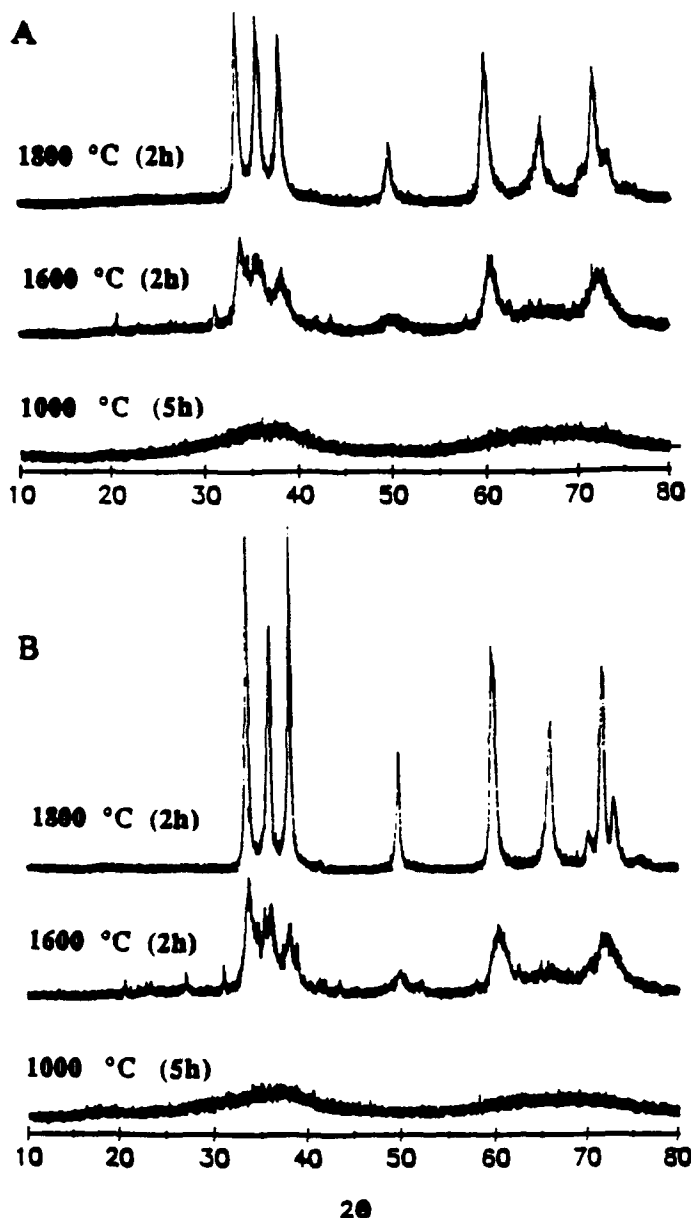


Figure 3. X-ray diffraction patterns of a) gradually pyrolyzed (GP) and b) rapidly pyrolyzed (RP) SiC/AlN precursor mixture.

The solid state NMR spectra of the solid solution samples (Figures 4-6) show the effects of the miscibility gap in the SiC/AlN solid solution below 1950 °C [27]. Thus, both 1000 °C samples show spectra consistent with expectations for "averaged" $\text{Al}(\text{Si})\text{N}_x\text{C}_y$ environments whereas, after crystallization of these samples at 1600-1800 °C, the the Al and Si NMR peaks shift to chemical shift values more nearly representative of the "pure" components, AlN and SiC. On the other hand, there are clearly differences in these spectra that support the presumption of solid solution

formation and suggest further that the processing method employed plays a role in determining the atomic-level homogeneity of the crystallized SiC/AlN solid solution phases obtained. In particular, after heating to 1000 °C the gradually pyrolyzed (GP) sample exhibits a two-peak ^{27}Al NMR spectrum, with one relatively sharp peak close to the expected position for pure AlN (Figure 4). This suggests that partial phase separation occurs during the slow heating of the precursor mixture, as would be expected on the basis of the lower thermal stability of $[\text{Et}_2\text{AlNH}_2]_3$ relative to HPCS [26]. Moreover, in the ^{29}Si NMR spectrum obtained for the rapidly pyrolyzed (RP) sample after heating to 1800 °C, the main Si peak is broader and shifted to a more shielded position relative to that observed for the corresponding GP sample (Figures 5 and 6). These data suggest that on an atomic level, the crystallized solid solution phases are slightly different, with the RP sample exhibiting a greater degree of homogeneity and a more "solid-solution like" ^{29}Si NMR spectrum.

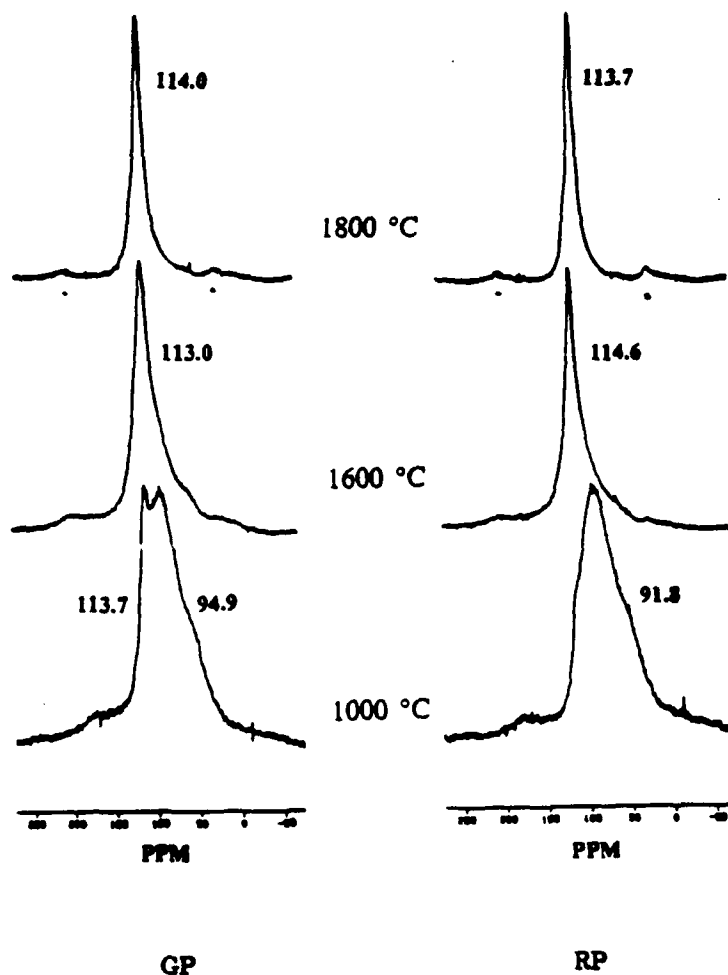


Figure 4. Solid state ^{27}Al MAS NMR spectra of the gradually pyrolyzed (GP) or rapidly pyrolyzed (RP) HPCS/ $[\text{Et}_2\text{AlNH}_2]_3$ precursor mixture.

Despite these subtle processing-dependant differences in composition and homogeneity and the presence of a miscibility gap in the phase diagram, the successful generation of 2H solid solutions of SiC and AlN from HPCS and $[\text{Me}_2\text{AlNH}_2]_3$ mixtures represents a significant advance in ceramic processing by polymer precursor pyrolysis. This opens up the possibility of using liquid phase, thermally curable precursors such as HPCS not only as a source of SiC coatings and matrices for ceramic composites, but also for the preparation of other mixed-component ceramic

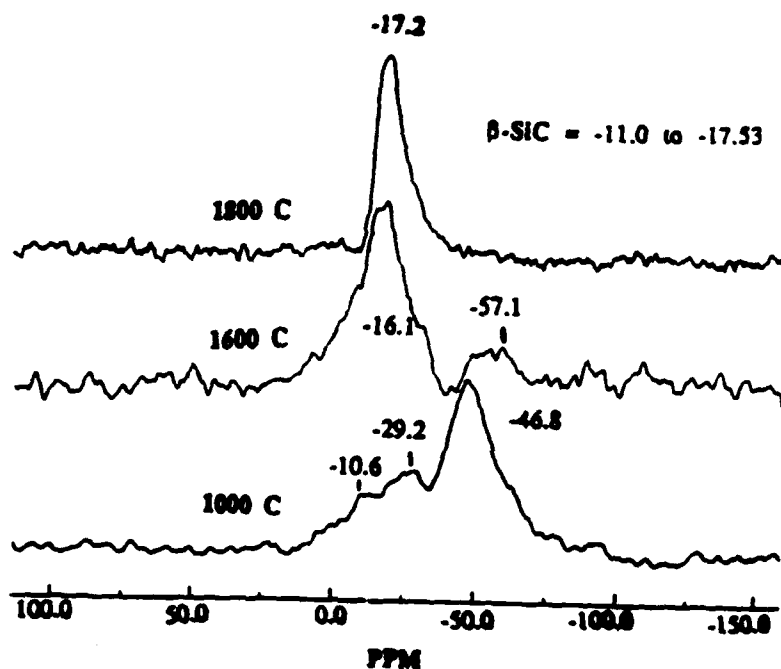


Figure 5. Solid state ^{29}Si MAS NMR spectra of a gradually pyrolyzed HPCS/(Et₂AlNH₂)₃ precursor mixture.

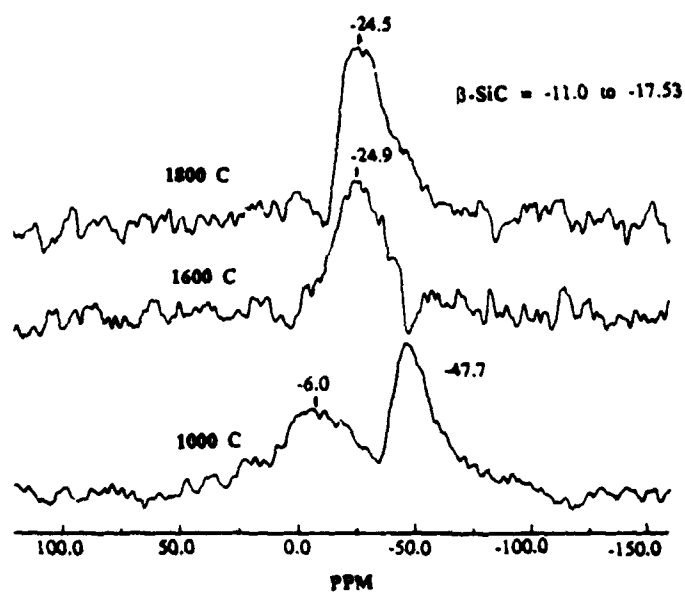


Figure 6. Solid state ^{29}Si MAS NMR spectra of a rapidly pyrolyzed HPCS/(Et₂AlNH₂)₃ precursor mixture.

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systems that may be more advantageous than SiC alone. In particular, in the case of SiC/AlN, the alloying of SiC with AlN has been reported to improve its microstructural stability, inhibiting the exaggerated grain growth that is known to contribute to the loss of strength typically observed for commercial "SiC" fibers at high temperatures (1200-1800 °C) [27]. The SiC/AlN solid solution has also been reported to have superior strength and oxidation resistance compared to either SiC or AlN alone [28].

We have also explored the use of both precursor mixtures and specially designed single-component precursors to prepare nanocrystalline composites of AlN/SiC, AlN/Si₃N₄, BN/Si₃N₄, AlN/BN, and BN/TiN [29]. We have demonstrated that such precursors can be used to obtain extremely fine-grained (typically less than 100 nm), homogeneously mixed composite powders of these crystalline ceramic phases. Moreover, these fine-grained mixtures resist coarsening during exposure to temperature in excess of 1500 °C. Such mixed-phase ceramics may be useful as matrices for SiC-reinforced composites, in applications requiring superplasticity, or as tough monolithic materials in their own right.

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